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COMMUNICATION

Optical electron transfer through 2,7-diethynylfluorene spacers in mixed-valent complexes containing electron-rich "(η^2-dppe)(η^5-C_5Me_5)Fe" endgroups†

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We report in this communication the study of the intramolecular electron transfer through a 2,7-diethynylfluorenyl spacer in the Fe(II)/Fe(III) mixed-valent (MV) complex [(η^2-dppe)(η^5-C_5Me_5)FeC≡C(2,7-$C_{21}H_{24}$)C≡CFe(η^5-C_5Me_5)(η^2-dppe)][PF_6] (1[PF_6]). The complex is generated *in situ* by comproportionation from its homovalent dinuclear Fe(II) and Fe(III) parents (1 and 1[PF_6]$_2$). It is shown that electronic delocalization is much more effective through a 2,7-fluorenyl than through a 4,4′-biphenyl bridging unit.

In the field of molecular electronics,[1–6] the understanding of structural features influencing the intramolecular electron transfer has become decisive for optimizing the design of smart molecular-sized devices.[7,8] While electron-transfer through several (hetero)aromatic units has been thoroughly investigated,[9] to our knowledge, no electronic coupling through 2,7-diethynylfluorenyl-based bridges has been reported so far. Indeed, among the various such dinuclear transition metal complexes reported,[10,11] most of them featured electron-poor metal centers and presented no other stable and isolable redox state(s), except perhaps for a few derivatives reported by Raithby and Wong.[12,13] But even in these cases, the properties of the mixed-valent state of these compounds were not investigated. In the frame of a project aimed at developing redox-switchable multiphotonic absorbers,[14–17] we recently synthesized the homovalent Fe(II) and Fe(III) compounds **1** and **1**[PF_6]$_2$ (Chart 1) featuring the electron-rich "(η^2-dppe)(η^5-C_5Me_5)Fe" endgroups.

We thus logically wondered about the intramolecular electron-transfer properties of the Fe(II)/Fe(III) mixed valent (MV) congener of these compounds (**1**[PF_6]).[1,8] Likewise to its 4,4′-biphenyl analogue (**2**[PF_6]) previously studied in our group[18] or to other related dinuclear carbon-rich MV derivatives,[7,19–21] **1**[PF_6] certainly constitutes another example of organometallic molecular wire.[8,9] In that respect, we have previously shown that a remarkably large electronic coupling ($H_{FeFe} \cong 145$ cm^{-1}) was operative between the redox-active endgroups of **2**[PF_6] in spite of the large intramolecular distance between them (*ca.* 16 Å).[18] The coplanarity of the fluorenyl unit, which should result in a better overlap of its π-manifold, is anticipated to increase the electronic coupling between the redox-active endgroups relative to a 4,4′-biphenyl spacer. However, the loss of axial symmetry with the 2,7-fluorene spacer might simultaneously result in detrimental quantum interferences.[22,23] Thus, in order to clearly establish how the electronic coupling is modified when progressing from **1**[PF_6] to **2**[PF_6], we have decided to experimentally determine H_{FeFe} for **1**[PF_6].

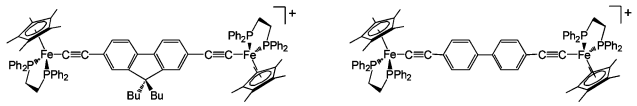
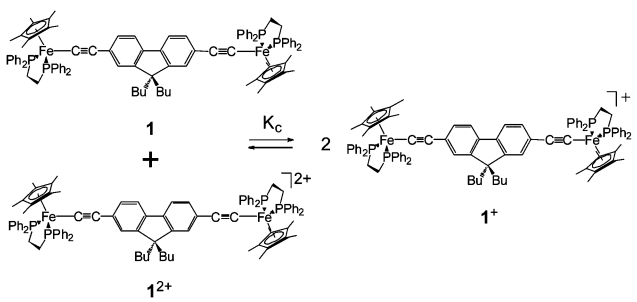


Chart 1

Given that a MV complex is always in equilibrium with its homovalent parents, we first wondered about the thermodynamic stability of **1**[PF_6] in the comproportionation equilibrium (Scheme 1).[24] Based on the well known eqn (1),[25] it was immediately apparent from the cyclic voltammogram of **1** (or **1**[PF_6]$_2$) that



Scheme 1

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† Electronic supplementary information (ESI) available: Synthesis of **1** and **1**[PF_6]$_2$. CIF file for **1**. Simulation procedure of the voltammogram used for **1**. UV and IR spectra obtained from equimolar mixtures of **1** and **1**[PF_6]$_2$. Solvatochromy and deconvolution of the near-IR absorption. CCDC reference number 694575. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10231a

the corresponding MV compound has not a sufficient stability to be quantitatively isolated by chemical oxidation of **1**, since the voltammogram exhibits strongly overlapping waves for the two stepwise (and chemically reversible) iron-centred oxidations (see ESI†). Moreover, when coming close together, the apparent potential difference between these redox waves does not match anymore with the real ΔE° value.[26] Accurate values of the corresponding redox potentials in dichloromethane were obtained by simulation of this voltammogram (–0.11 and –0.22 V *vs.* ECS) and a thermodynamic equilibrium constant (K_c) of 76 ± 8 could be derived for this comproportionation reaction at 25 °C from the difference between these redox potentials (ΔE° = 111 ± 3 mV).

$$(RT/F)\log(K_c) = \Delta E^\circ \quad (1)$$

Notably, this potential separation is significantly larger than that previously determined for **2**[PF_6] (62 mV), in line with a larger electronic interaction taking place between the redox endgroups in **1**[PF_6], which also translates in a larger stability constant for this MV complex (a K_c value of 11 had been found for **2**[PF_6]). While ensuring a good solubility of the compound, the two butyl chains on the fluorene spacer possibly contribute to increase ΔE° by limiting any pi-stacking or ion pairing in solution (Fig. 1). Interestingly, when the cyclic voltammetry is repeated in acetone, the separation between the redox waves is hardly discernible, indicating a much smaller comproportionation constant in this solvent possessing a higher dielectric constant. Under these conditions, simulation is needed to derive ΔE° and a K_c value of 28 ± 6 can be found for **1**[PF_6] in acetone.

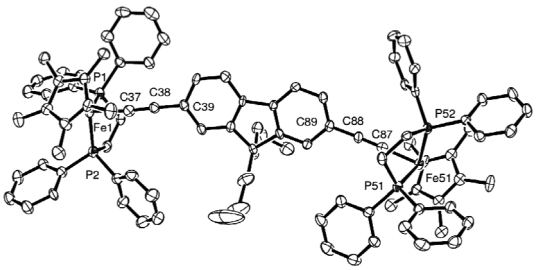

Fig. 1 ORTEP of **1** (50% probability level).

In order to study **1**[PF_6] in CH_2Cl_2, the mixed valent complex was generated after solubilizing equimolar quantities of **1** and **1**[PF_6]$_2$ in this solvent.[27,28] According to the K_c value found, **1**[PF_6] will be present in 81% in solution along with 9.5% of **1** and 9.5% of **1**[PF_6]$_2$. The infrared spectrum of this medium in the 1900–2000 cm^{-1} range reveals the presence of two new strong $\nu_{Fe-C\equiv C}$'s overlapping the corresponding modes of **1** and **1**[PF_6]$_2$ (ESI†). These absorptions, typical of Fe(II)-C≡C and a Fe(III)-C≡C acetylides, evidence the presence of distinct and localized redox sites in **1**[PF_6].[29] Also, after thawing an equimolar mixture of **1** and **1**[PF_6]$_2$ in CH_2Cl_2/1,2-$C_2H_2Cl_2$, a rhombic signal can be detected by ESR at 77 K (g_1 = 1.983, g_2 = 2.035 and g_3 = 2.380). The latter is typical of a low-spin Fe(III)-centred radical in cationic piano-stool acetylide complexes.[30] In accordance with the voltammetric study, these data establish **1**[PF_6] as a Class-II MV compound in the classification of Robin and Day.[31,32]

We next turned our attention to the electronic absorptions of **1**[PF_6]. In the UV-vis range, the equimolar mixture between **1** and **1**[PF_6]$_2$ reveals a spectrum resembling that of the parent homovalent complexes. However, several among the most intense transitions are shifted relative to these detected for pure **1** and **1**[PF_6]$_2$, in line with the presence of **1**[PF_6] in the medium. Then, in the near-IR range, an intense and *new* absorption is detected at *ca.* 5075 cm^{-1} which was absent for pure solutions of **1** and **1**[PF_6]$_2$. Actually, **1** is silent in this spectral range, whereas **1**[PF_6]$_2$ presents only a very weak absorption at 5423 cm^{-1} (ε = 410 M^{-1} cm^{-1}) corresponding to a forbidden ligand field (LF) transition.[18,30] The broad absorption at 2000 nm is thus diagnostic of the MV complex **1**[PF_6]. Considering the energy ($\tilde{\nu}_{max}$ = 4995 cm^{-1}) of the maximum, the halfwidth [$(\tilde{\nu}_{1/2})_{exp}$ > 6000 cm^{-1}] and also the (non-gaussian) shape of this band (Fig. 2), it cannot correspond to a single intervalence charge transfer (IVCT) band (see eqn (2)) but most likely results from several overlapping sub-bands.

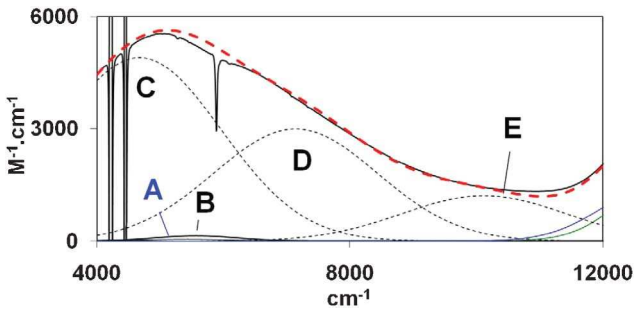

Fig. 2 Near-IR spectra for an equimolar mixture of **1** and **1**[PF_6]$_2$ in dichloromethane (1.3 10^{-4} M in total) and proposed de-convolution (sub-bands A–E: see text). Apparent extinction coefficients (0.81×ε) are given in ordinate.

The near-IR band was then deconvoluted into several Gaussian sub-bands (ESI†). One evident contribution (A) corresponds to the weak ligand LF transition of **1**[PF_6]$_2$ present in the medium (9.5%), but its impact on the band shape is negligible. Another contribution (B) certainly originates from a similar LF transition taking place on the Fe(III) site of **1**[PF_6].[33] Again this sub-band should not be strongly influencing the band shape of the near-IR transition detected for the MV complex. Actually, (at least) three much more intense contributions need to be considered to properly reproduce the observed band shape (C–E). Notably, three such sub-bands were often considered in near-IR band deconvolutions for related organoiron MV derivatives.[18,34,35] For MV complexes possessing an unpaired electron on metal d sub-levels lying close in energy to the HOMO-1/HOMO-2 levels, in pseudo-octahedral environments, when a sizable metal–metal interaction is mediated by the bridging ligand, these might be associated with the sought IVCT and two interconfigurational transitions.[36] Thus, similarly to what we did with the MV complex (η^2-dppe)(η^5-C_5Me_5)FeC≡C(1,4-C_6H_4)C≡CFe(η^5-C_5Me_5)(η^2-dppe) (**3**[PF_6]),[18,30] the most intense sub-band at lowest energy (C) was considered to correspond to the IVCT transition. In line with this hypothesis, this sub-band (along with D and E) is hypsochromically shifted when the dichloromethane solvent is changed for a solvent with a higher dielectric constant such as acetone or acetonitrile. This observation allows us to refine further the classification of the **1**[PF_6] as a Class-IIA MV complex.

$$(\tilde{\nu}_{1/2})_{theo} = (2310.\ \tilde{\nu}_{max})^{1/2} \quad (2)$$

$$H_{ab} = (2.06 \times 10^{-2}/d_{ab})(\varepsilon_{max}\ \tilde{\nu}_{max}\ \Delta\tilde{\nu}_{1/2})^{1/2} \quad (3)$$

The sub-bands C–E were considered to have similar halfwidths in the deconvolution procedure,[31] with $\tilde{\nu}_{1/2}$ constrained to remain close to the theoretical value predicted by the Hush theory (eqn (2)).[37,38] A fair fit can be obtained by this approach (Fig. 2), yielding a sensible reorganisation energy for the IVCT ($\lambda \approx 4670$ cm^{-1}; $\tilde{\nu}_{1/2} = 3050$ cm^{-1}; $\varepsilon = 6050$ M^{-1} cm^{-1}) and sensible transition energies for the two interconfigurational processes D and E (7140 cm^{-1} and 10100 cm^{-1}).[18]

Finally, using the classic Hush equation (eqn (3)), a H_{FeFe} value of *ca.* 380 cm^{-1} was derived for **1**[PF$_6$] from the energy, intensity and halfwidth of the sub-band C (IVCT). These electronic couplings are quite important for two metal centres located *ca.* 16 Å apart (Fig. 1).[9,39] This nanoscopic distance outlines further the strong delocalization of the unpaired electron–hole in this organometallic MV compound. In line with established trends,[25,40] the larger H_{FeFe} value found for **1**[PF$_6$] relative to **2**[PF$_6$], confirms our initial belief that the co-planarity of the central aromatic spacer is beneficial to the electronic communication. This rather large H_{FeFe} value found for **1**[PF$_6$], along with the intensity of its IVCT absorption, is reminiscent of signatures usually observed for more strongly coupled MV complexes (Class-IIB), such as **3**[PF$_6$] previously mentioned.[18]

In conclusion, we have established here that the 2,7-fluorenyl spacer allows us to significantly improve the electronic communication between the [(η^2-dppe)(η^5-C$_5$Me$_5$)Fe]$^{n+}$ (n = 0,1) redox-active endgroups compared with the 4,4′-diethynylbiphenyl spacer in the corresponding MV complexes. In dichloromethane, when compared with **2**[PF$_6$], this translates in a large increase of the comproportionation constant (K_c) of **1**[PF$_6$] (Scheme 1) and in a smaller improvement (2.6 fold) of the electronic coupling between the redox endgroups. However, according to the H_{FeFe} value(s) found, the end-to-end electron transfer is now clearly adiabatic for **1**[PF$_6$] ($H_{FeFe} \geq 200$ cm^{-1}),[41] and becomes much faster than in the Class-IIA MV analogue **2**[PF$_6$].

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